**Australian** Journal of **Basic and Applied Sciences**

AENSI Publisher

**AJBAS**
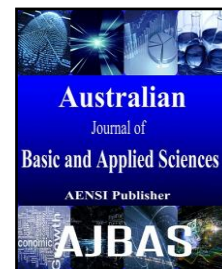
# Oxidative dehydrogenation of propane on Pd-Mo/γ-Al2O3 catalyst: a kinetic study.

[1]Hugo Zea and [2]Luis Carballo

[1]*Departamento de Ingeniería Química y Ambiental, Facultad de Ingeniería, Universidad Nacional de Colombia, Carrera 30 Numero 45-03, Edificio 412, of 201, Bogotá, Colombia*
[2]*2Departamento de Ingeniería Química y Ambiental, Facultad de Ingeniería, Universidad Nacional de Colombia, Carrera 30 Numero 45-03, Edificio 453, of 301, Bogotá, Colombia*

**A R T I C L E   I N F O**

**A B S T R A C T**

The increasing demand of propylene to be used as raw material for the production of important chemicals products requires the development of efficient chemical routes for its synthesis. The oxidative dehydrogenation of propane to propylene (ODHP) has been proposed as a thermodynamically favorable route for the production of propylene from propane. In this study a simplified Mars Von Krevelen mechanism (MVK) was used to describe the kinetics mechanism of the ODHP reaction catalyzed by a bimetallic 1.25% of Pd and 3.75% Mo (weight percentage) supported on alumina catalyst over a wide range of compositions, temperatures and flow conditions. The kinetic rate equation with the best fitting to experimental data corresponds to one in which the propane adsorption is the controlling step.

## INTRODUCTION

The increasing demand of propylene to be used as raw material for the production of polypropylene, acrolein, propylene oxide and cumene among other important chemicals products requires the development of efficient chemical routes for its synthesis (Lobera *et al*. 2008). The oxidative dehydrogenation of propane to propylene (ODHP) has been proposed as a thermodynamically favorable route for the production of propylene from propane (equation 1).

$$C_3H_8 + 0.5O_2 \leftrightarrow C_3H_6 + H_2O \qquad (1)$$
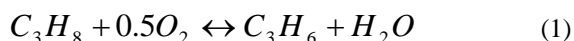
ODHP is an equilibrium limited reaction, it is generally carried out at 450–650 $^\circ$C and atmospheric pressure using supported noble metals as palladium, platinum or chromium as catalyst (Gascon *et al*. 2003). It has been reported that adding modifiers such molybdenum, tin, arsenic and lead improves catalyst activity and stability by inhibiting side reactions as isomerization and hydrocracking (Bhasin *et al*. 2001). Pt catalyst includes promoters such alkali metals and alkaline earth metal to reduce support acidity, increase Pt dispersion and reduce Pt sintering (den Otter and Dautzenberg 1978;

Rodriguez *et al*. 2005; Zhang *et al*. 2013). Adding a second metal have a profound effect on Pd supported catalyst activity and selectivity by inducing structural changes (Chaar *et al*. 1987; Kung and Kung 1992; Lee *et al*. 1997; Stern and Grasselli 1997; Baldi *et al*. 1998; Soczyaski *et al*. 1999). There have been reports of highly active and selective catalytic systems for the ODHP reaction dehydrogenation constituted by elements of group VIII promoted with Mo; in a previous study (Zea *et al*. 2011) the performances of Pd/γ-Al2O3, Mo/γ-Al2O3, and Pd-Mo/γ-Al2O3 catalysts were investigated in the ODHP reaction in order to understand the effect of the Pd-Mo interaction in terms of structural properties and catalytic activity. The Pd-promoted Mo catalyst showed lower dispersion values but a significantly higher specific activity to the formation of propylene when compared to the monometallic Pd catalyst under similar reaction conditions. In this study a simplified Mars Von Krevelen mechanism (MVK) was used to describe the kinetics mechanism of the ODHP reaction catalyzed by a bimetallic 1.25% of Pd and 3.75% Mo (weight percentage) supported on alumina catalyst over a wide range of compositions, temperatures and flow conditions.

**Corresponding Author:** Hugo Zea, Departamento de Ingeniería Química y Ambiental, Facultad de Ingeniería, Universidad Nacional de Colombia, Carrera 30 Numero 45-03, Edificio 412, of 201, Bogotá 111141, Colombia;
E-mail: hrzear@unal.edu.co.

## MATERIALS AND METHODS

### *Catalysts Synthesis:*

Bimetallic 1.25 Pd and 3.75 Mo percentage on weight supported on gamma-alumina (1.25Pd3.75Mo) catalysts were prepared by wet co-impregnation. The support used was γ-alumina (Alpha-Aesar ,surface area: 79 $m^2$/g, pore volume: 0.31 $cm^3$/g); it was impregnated with an aqueous solutions of palladium chloride ($PdCl_2$) and ammonium heptamolybdate ($[NH_4]Mo_7O_{24}.6H_2O$) to generate the proper metallic load as described in detail elsewhere (Zea, Figueiredo *et al*. 2011). After impregnation, the catalyst was heated from room temperature to 450 $^o$C (5 $^o$C/min) in dry air atmosphere (70 ml/min); the 450 $^o$C temperature was kept for 120 minutes then increased to 600 $^o$C (5 $^o$C/min) and kept at this temperature for 240 minutes, then natural cooling was allowed; catalysts was stored in an inert atmosphere (He) to avoid its degradation.

### *Catalytic Activity:*

ODHP catalytic activity on the 1.25Pd3.75Mo catalyst was measured in a fixed bed flow stainless steel reactor (6.3 mm internal diameter) containing 100 mg of oxidized catalyst sample (particle size between 200 – 250 microns) and coupled directly to a gas chromatograph. Propylene, carbon monoxide and dioxide were found to be the main reaction products. Propane conversion (X) and propylene selectivity (S) were evaluated at three temperatures (400, 450 and 500 $^o$C), varying the ratio of oxygen/propane (U) in the feed to evaluate catalytic activity in the stoichiometric condition (U=1), below stoichiometric condition (U=0.5) and above

stoichiometric condition (U=2) as a function of the feed ratio W/Feed $C_3H_8$ (grams of catalyst/$C_3H_8$ moles). The reaction mixture (100 ml/min) contained propane, oxygen and helium as balance gas, flows rate were controlled using Bronkhorst High-Tech series F-200 and F201 mass flow meters. Preliminary experiments indicated the absence of mass transfer restrictions for the reaction conditions.

## RESULTS AND DISCUSSION

Results of the catalytic activity data for the bimetallic 1.25Pd3.75Mo catalyst in terms of the variation of propane conversion (X) and selectivity to Propylene (S) as a function of feed ratio (W/Feed $C_3H_8$) for various oxygen/propane (U) ratios are presented in Figures 1, 2 and 3. Figure 1 shows the results obtained at 400 $^o$C. It can be observed the reduction tendency in selectivity as the reaction conversion increases. The experiment done below stoichiometric and at stoichiometric conditions (U=0.5 and U=1, respectively) shown overlapping similar profiles of the conversion as the feed ratio increases. Conversion data obtained for feed ratio above stoichiometric condition (U=2) has comparable values at lowest feed ratio, however as the feed ratio value increases the conversion increases faster than in the U=0.5 and U=1 experiments, with values up to 1.5 times higher. Figure 1 also shows the important effect the feed ratio has on the reaction selectivity; the selectivity profiles for the case of the conditions (U=2 and U=0.5) are substantially lower than the values obtained for U=1 condition, being in average 2.2 and 1.4 times higher than the values obtained for the non-stoichiometric conditions, respectively.
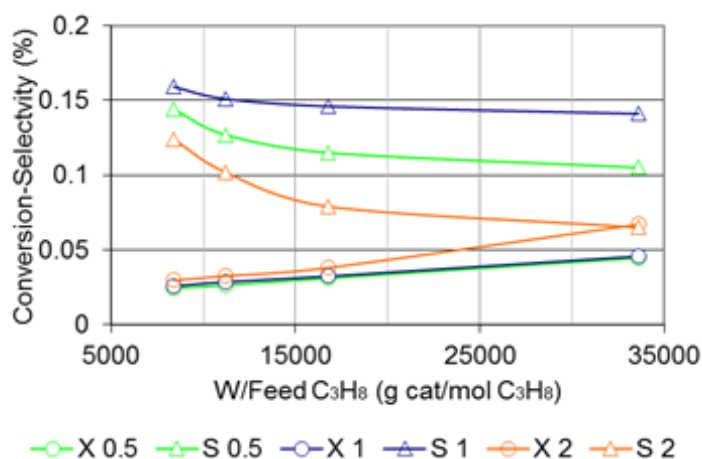


**Fig. 1:** Conversion and selectivity as function of feed ratio (W/Feed $C_3H_8$) and the ratio of oxygen/propane (U) at 400 $^o$C

Figure 2 shows the change of propane conversion (X) and selectivity to Propylene (S) as a function of feed ratio (W/Feed $C_3H_8$) for various

oxygen/propane (U) ratios for the 450 $^o$C experiments. The tendency of selectivity reduction as conversion increases is still observed in these

experiments; conversion values reported for the 450 $^o$C are higher than the obtained for the 400 $^o$C experiments, although the U=0.5 and U=1 conditions still follow a very close behavior there a clear separation showing U=1 with higher conversion; in the case of the conversion for the U=2 condition the increment compared to its counterpart at 400 $^o$C is even higher, almost twice as the values reported for the 400 $^o$C. The selectivity values reported for the 450 $^o$C are higher than the one obtained for the 400 $^o$C experiments. Selectivity is not longer higher for the U=1 condition as observed in the 400 $^o$C, being overpass by the U=0.5 condition; selectivity of the U=0.5 condition is in average 2.3 and 1.12 higher than the selectivity obtained for the U= 1 and U=2 respectively, this factor are closed to the ones calculated for the 400 $^o$C experiment.
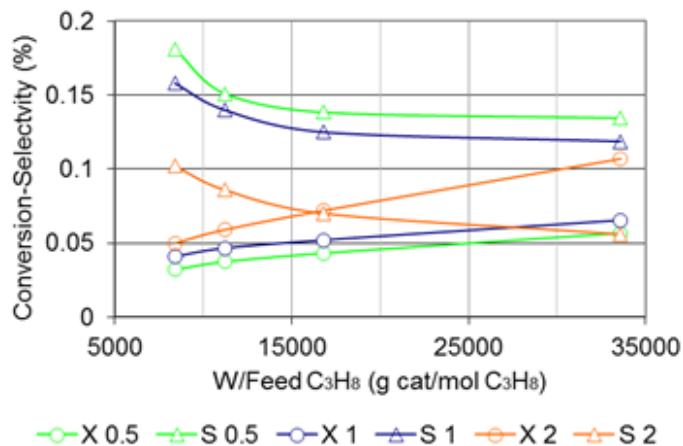


**Fig. 2:** Conversion and selectivity as function of feed ratio (W/Feed $C_3H_8$) and the ratio of oxygen/propane (U) at 450 $^o$C

Figure 3 shows the change of propane conversion (X) the selectivity to Propylene (S) as a function of feed ratio (W/Feed C3H8) for different values of oxygen/propane (U) ratios for the 500 $^o$C experiments. The opposed profile behaviors of selectivity and conversion continued; conversion of the U=2 condition shows higher values than the obtained for the U= 1 and U= 0.5 conditions. In term of selectivity changes, the catalyst evaluated at the U=0.5 condition does not present the highest values as observed for the experiment performed at 450 $^o$C, instead the U=1 condition generates the highest selectivity values when compared to the U=0.5 and U=2 conditions. The U=1 condition selectivity is a lot higher than the selectivity for the condition U=2 and U=0.5; this strong dependency of catalysts selectivity as a function of the Oxygen/Propane ratio in the reactor feed is a clear indication that the reaction selectivity is strongly dependent of the amount of oxygen available in the reaction mixture. The selectivity of the U=1 is in average 1.29 and 1.78 times higher than the values obtained at the U=0.5 and U=2 conditions.



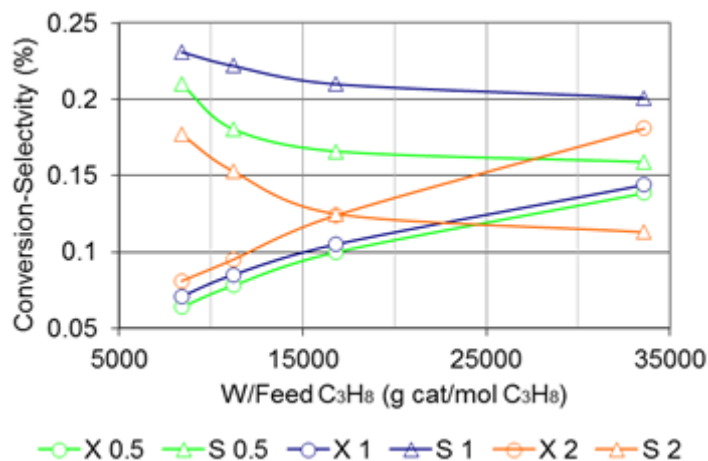**Fig. 3:** Conversion and selectivity as function of feed ratio (W/Feed $C_3H_8$) and the ratio of oxygen/propane (U) at 500 $^o$C

In a previous study (Zea, Figueiredo *et al*. 2011), the 1.25Pd3.75Mo catalyst was characterized using TEM coupled with EDS; the results clearly showed how the coimpregnation procedure of Pd and Mo results in a catalyst with individual Pd particles along with a well-dispersed Mo in the vicinity of them; XRD profile presented the PdO peak however its position was slightly shifted to the left, indicating a possible weak interaction between the Pd and Mo. No clear evidence of the formation of a Pd-Mo alloy or solid solution was observed.

A simplified Mars Van Krevelen (MVK) reaction mechanism involves the propane adsorption on the PdO species, once adsorbed the propane molecule interact with the oxygen of the PdO specie breaking C-H bounds, generating a C=C bound and desorbing as propylene and water leaving on the surface a reduced active site, this reduced surface site is oxidized by the oxygen presented in the homogeneous phase. A schematic representation of the mechanism is shown:

$$A + X \leftrightarrow AX \qquad (2)$$

$$AX \leftrightarrow X_{red.} + R + S \qquad (3)$$

$$X_{red.} + B \leftrightarrow X \qquad (4)$$

Where A corresponds to propane, B to oxygen, R to propylene and S water to molecules; X corresponds the active sites of the catalysts surface and AX corresponds to the surface specie formed by the adsorption of propane on the active site. Equation (2) represents propane adsorption on an active site, equation (3) represents the reaction of the propane adsorbed on the active site to from propylene and water, finally equation (4) represents the oxidation of the reduce active site generate during the reaction described in equation (3), this oxidation is done with the oxygen available in the homogenous phase.

Three kinetic rate equations can be proposed applying the concept of controlling step; equation (5), (6) and (7) correspond to the cases in which propane adsorption is the controlling step, the superficial reaction is the controlling step and the reoxidation of the reduced active site is the controlling step, respectively.

$$R_A = \frac{k_A \left(Y_A - Y_R * Y_S\right) / \left(K * Y_B^{1/2}\right)}{\left(1 + K_A * Y_R * Y_S / K * Y_B^{1/2} + K_B * Y_B^{1/2}\right)} \qquad (5)$$

$$R_A = \frac{k_{sr} * K_A * K_B \left(Y_A * Y_B^{1/2} - Y_R * Y_S / K\right)}{\left(1 + K_A * Y_A + K_B * Y_B^{1/2}\right)^2} \qquad (6)$$

$$R_A = \frac{k_B \left(Y_B^{1/2} - Y_R * Y_S / K * Y_A\right)}{\left(1 + K_A * Y_A + K_B * Y_R * Y_S / K * Y_A\right)^2} \qquad (7)$$

Where $k_A$ and $k_B$ are the kinetic constants of adsorption of the specie A and B, $k_{sr}$ is the surface reaction kinetic constant, $K_A$ and $K_B$ are the adsorption equilibrium constants for specie A and B, and K is the reaction equilibrium constant. Propane conversion data as function of the feed ratio (W/Feed $C_3H_8$) shows the reactors behaves as a differential reactor, the activity catalytic data obtained are adjusted by means of error minimization methods to the reaction kinetic equations (5), (6) and (7) (Chaar, Patel *et al*. 1987; Blasco and Nieto 1997; Jalowiecki-Duhamel *et al*. 1997; Stern and Grasselli 1997; Khodakov *et al*. 1998).

The kinetic rate equation with the best fitting to experimental data obtained for the 1.25Pd3.75Mo catalyst corresponds to one with the propane adsorption as controlling step, equation (5). The results of the experimental kinetics values and the values calculated from the fitted equation are show in Figures 4, 5 and 6 for the 400, 450 and 500 °C temperatures.
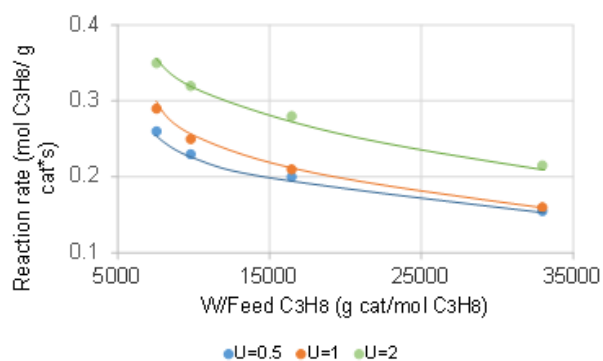


**Fig. 4:** Reaction rate as function of feed ratio (W/Feed $C_3H_8$) and the ratio of oxygen/propane (U) at 400 °C

Continuous lines in Figures 4, 5 and 6 represents the reaction rate calculated form the adjusted equation, average error form experimental and calculated data is below 2%. Kinetics and equilibrium constants, adsorption enthalpy, and heat of adsorption are obtained from Vant Hoff equation

$$k_A = 6.32 \times 10^8 e\left(-9987.97/T\right) \quad (6)$$

$$K_A = 9.99 \times 10^{14} e\left(13237.06/T\right) \quad (7)$$

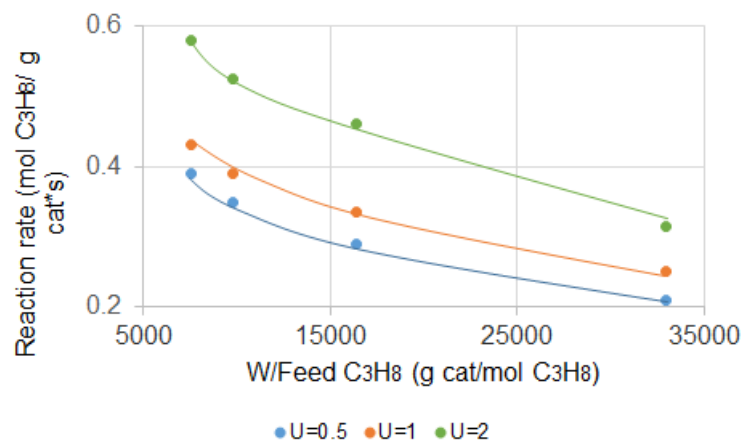$$K_B = 1.26 \times 10^4 e\left(14560.77/T\right) \quad (8)$$



**Fig. 5:** Reaction rate as function of feed ratio (W/Feed $C_3H_8$) and the ratio of oxygen/propane (U) at 450 $^o$C
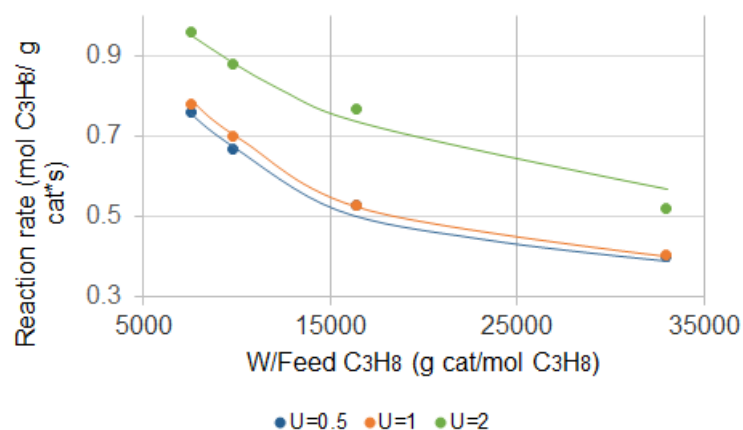


**Fig. 6:** Reaction rate as function of feed ratio (W/Feed $C_3H_8$) and the ratio of oxygen/propane (U) at 500 $^o$C

The standard enthalpy change of the propane adsorption on the active site is -110 kj/adsorbed mol. ODHP is a highly exothermic reaction enthalpy ( $\Delta H^o$ at 420 $^o$C is 2116.7 kJ/mol] and irreversible process ($\Delta G^o$ at 420 $^o$C is 2176.1 kJ/mol) where the selectivity to propylene is limited by the oxidative process leading to thermodynamically stable $CO_x$ species. From the kinetic point of view, the ODHP reaction is generally described by a set of parallel-consecutive reaction system, where both the selective reaction to propylene and its oxidation to $CO_x$ species and the parallel direct formation of $CO_x$ species are included. Many literature data report that $CO_x$ is formed mainly by consecutive oxidation of propylene and to a lesser extent on parallel path by direct oxidation of propane (Lemonidou 2001; Schindler *et al.* 2001; Rubio *et al.* 2003).

*Conclusions:*
Propane conversion and selectivity to propylene on bimetallic 1.25% of Pd and 3.75% Mo (weight percentage) supported on alumina catalyst were evaluated as function of feed ratio (W/Feed $C_3H_8$), ratio of oxygen/propane (U) and temperature. The results show a strong effect of the oxygen/propane ratio both on conversion and selectivity. Higher concentration of oxygen in the reactor feed increases propane conversion, but reduces propylene selectivity, the best performance of selectivity as a function of the ratio of oxygen/propane (U) was at

the stoichiometric condition (U=1). Propane conversion increases as the feed ratio (W/Feed $C_3H_8$) increases, on the contrary propylene selectivity decreases as the feed ratio (W/Feed $C_3H_8$) increases; both behaviors are properly adjusted by a simplified Mar Van Krevelen (MVK) mechanism where higher coverage of the adsorbed propane on the catalyst surface and a higher pressure of oxygen on the homogenous phase would be beneficial to yields a higher reaction rate, this trend is well describe for all the reaction temperatures, (W/Feed $C_3H_8$) feed ratios and the (U) oxygen/propane ratios.

## REFERENCES

Baldi, M., E. Finocchio, *et al.*, 1998. "Evaluation of the mechanism of the oxy-dehydrogenation of propane over manganese oxide." Applied Catalysis A: General., 173(1): 61-74.

Bhasin, M.M., J.H. McCain, *et al.*, 2001. "Dehydrogenation and oxydehydrogenation of paraffin to olefins." Applied Catalysis A: General., 221(1-2): 397-419.

Blasco, T. and J.M.L. p. Nieto, 1997. "Oxidative dyhydrogenation of short chain alkanes on supported vanadium oxide catalysts." Applied Catalysis A: General., 157(1): 117-142.

Chaar, M. A., D. Patel, *et al.*, 1987. "Selective oxidative dehydrogenation of butane over VMgO catalysts." Journal of Catalysis., 105(2): 483-498.

den Otter, G.J. and F.M. Dautzenberg, 1978. "Metal-support interaction in PtAl2O3 catalysts." Journal of Catalysis, 53(1): 116-125.

Gascon, J., C. Tellez, *et al.*, 2003. "Propane dehydrogenation over a Cr2O3/Al2O3 catalyst: transient kinetic modeling of propene and coke formation." Applied Catalysis A: General., 248(1-2): 105-116.

Jalowiecki-Duhamel, L., A. Ponchel, *et al.*, 1997. Oxidative dehydrogenation of propane on CeNiXOYmixed oxides hydrogen acceptors. Studies in Surface Science and Catalysis, Elsevier., 110: 383-392.

Khodakov, A., J. Yang, *et al.*, 1998. "Structure and properties of vanadium oxide-zirconia catalysts for propane oxidative dehydrogenation." Journal of Catalysis, 177(2): 343-351.

Kung, M.C. and H.H. Kung, 1992. "The effect of potassium in the preparation of magnesium orthovanadate and pyrovanadate on the oxidative dehydrogenation of propane and butane." Journal of Catalysis, 134(2): 668-677.

Lee, K.H., Y.S. Yoon, *et al.*, 1997. "An evidence of active surface MoOx over MgMoO4 for the catalytic oxidative dehydrogenation of propane." Catalysis Letters, 46(3-4): 267-271.

Lemonidou, A.A., 2001. "Oxidative dehydrogenation of C4 hydrocarbons over VMgO catalyst kinetic investigations." Applied Catalysis A: General, 216(1): 277-284.

Lobera, M.P., C. Tellez, *et al.*, 2008. "Transient kinetic modelling of propane dehydrogenation over a Pt-Sn-K/Al2O3 catalyst." Applied Catalysis A: General, 349(1-2): 156-164.

Rodriguez, D., J. Sanchez, *et al.*, 2005. "Effect of tin and potassium addition on the nature of platinum supported on silica." Journal of Molecular Catalysis A: Chemical, 228(1-2): 309-317.

Rubio, O., J. Herguido, *et al.*, 2003. "Oxidative dehydrogenation of n-butane on V/MgO catalysts kinetic study in anaerobic conditions." Chemical Engineering Science, 58(20): 4619-4627.

Schindler, G. t.-P., T. Ui, *et al.*, 2001. "Kinetics of isobutene selective oxidation over Mo-V-P-As-Cs-Cu-O heteropoly acid catalyst." Applied Catalysis A: General, 206(2): 183-195.

Soczyaski, J., J. Ziakowski, *et al.*, 1999. "Oxidative Dehydrogenation of Propane on NixMgxAl2O4 and NiCr2O4 Spinels." Journal of Catalysis, 187(2): 410-418.

Stern, D.L. and R.K. Grasselli, 1997. "Propane Oxydehydrogenation over Molybdate-Based Catalysts." Journal of Catalysis, 167(2): 550-559.

Zea, H., J. Figueiredo, *et al.*, 2011. "Promoting effect of mo on Pd / gamma-Al2O3 supported catalysts in the oxidative dehydrogenation of propane." Dyna, 78(170): 159-166.

Zhang, Y., Y. Zhou, *et al.*, 2013. "Effect of magnesium addition on catalytic performance of PtSnK/Al2O3 catalyst for isobutane dehydrogenation." Fuel Processing Technology, 92(8): 1632-1638.